III.E.8 Feasibility of a SOFC Stack Integrated Optical Chemical Sensor

Objectives

- Design of thermally stable nano-cermets using radio frequency magnetron sputtering techniques
- Synthesis of nano-cermets with a narrow particle diameter distribution
- Probe Au nanoparticle surface plasmon resonance (SPR) properties and Pd-YSZ (yttria-stabilized zirconia) optical properties as a function of temperature and chemical exposure

Approach

- Synthesis of Au-YSZ nano-cermets using physical vapor deposition techniques
- Characterize Au nanoparticles using optical and microstructural analytical techniques
- Testing of thermal stability (500-1000°C) of nano-cermets and their corresponding optical properties
- Determine the thermal and chemical stability (CO, NO_2, hydrogen) of nano-cermets and the corresponding optical properties

Accomplishments

- The detection of CO using all-optical techniques was demonstrated at an operating temperature of 500°C in the presence of an air carrier gas

Future Directions

- Evaluate the long term stability of the Au-YSZ films towards both temperature and CO exposures
- Characterize the CO sensing capabilities of the Au-YSZ films as a function of oxygen background pressure, temperature and Au content
- Evaluate the sensing properties of the Au-YSZ tailored nanocomposite films for the detection of sulfur compounds, H_2 and NO_2

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Introduction

The DOE-NETL Innovative Concepts Phase II Program is investigating the feasibility of harsh environment compatible chemical sensors based on monitoring the surface plasmon resonance (SPR) bands of metal nanoparticle doped YSZ nano-cermets, as a function of fuel concentrations, impurities e.g. CO and temperature (500-900°C). In particular, Au nanoparticles exhibit a strong SPR band whose shape and spectral position is not only highly dependent on the refractive index of the host medium but also on chemical reactions at the interface between the metal and the surrounding environment.[1]

In this report, the operational range of Au nanoparticle based sensing of CO was extended up to 500°C through the use of a materials system comprised of Au nanoparticles embedded in an yttria-stabilized zirconia (YSZ) matrix. A reversible change in the optical properties of this nanocomposite is observed upon exposure to gas cycles of air and an air/CO mixture. The sensing mechanism has been attributed to high temperature interfacial charge transfer chemical reactions, occurring at the perimeter of the Au nanoparticles, which inject charge into the Au nanoparticle causing changes in both the position and shape of the SPR band. These reactions are presumed to be associated with the reduction of the YSZ matrix and the oxidation of CO, via a charge transfer reaction between YSZ bound oxygen anions, formed through the dissociative adsorption of oxygen molecules on YSZ at high temperatures, and the Au nanoparticles.

Approach

The Au-YSZ nanocomposite films are deposited using dual target confocal physical vapor deposition, with the metal and metal oxide sputtering gun deposition rates tuned to achieve the desired metal-to-metal oxide composition. Thermal annealing in argon at temperatures above their respective operating temperatures is used both to thermally stabilize the films and also to grow nanoparticles of a given size. Materials characterization of the films using scanning electron microscopy (SEM), Auger spectroscopy, Rutherford backscattering spectroscopy (RBS) and x-ray diffraction (XRD) analyses is used to determine the microstructural and composition properties. Ex situ optical characterization using ultraviolet to

[1]Kreibig, U.; Vollmer, M.; *Optical Properties of Metal Clusters*; Springer, New York, 1995.

visivle (Uv-Vis) absorption spectroscopy and spectro-ellipsometric analysis is used to correlate the material properties with the resulting optical properties. In situ Uv-Vis spectroscopy utilizing a charge-coupled device (CCD)-based detection system as a function of both temperature and chemical exposure is used to determine the gas sensing properties with a time resolution on the seconds scale. Test gases include, CO, NO_2 and hydrogen which will provide a range of reducing and oxidizing environments whose absorption spectra effects combined with theoretical calculations will help deconvolute changes in both the dielectric and the chemical environment surrounding the bimetallic and metallic nanoparticles.

Results

Figure 1a displays the absorption spectrum along with a corresponding Lorentzian fit to the data for a representative Au-YSZ film in the spectral region between 470 and 920 nm at 500°C in an air background. Noise levels at the longer wavelength limit of the spectrum become rather pronounced due to the incomplete removal of the Xe lines from the absorption spectrum. The SPR band peaks at approximately 600 nm and was fitted to a Lorentzian curve, with an R^2 value of 0.998, in the region between 560 and 800 nm, to extract the changes in the spectrum upon exposure to the air/CO mixture. This fitting range was dictated at the shorter wavelengths by the Au interband transitions which have an onset at approximately 520 nm, while wavelengths longer than 800 nm were ignored due to the pronounced noise levels. Figure 1b displays the absorption spectra of the Au-YSZ nanocomposite for both the air and an air/CO (1 vol.%) gas mixture. In both cases, a SPR absorption band at approximately 600 nm was observed. However, upon exposure to CO, the SPR band slightly blue shifts and becomes narrower, with no measurable change in the baseline of the spectrum at the short and long wavelength limits. The inset of Figure 1b displays the difference spectrum obtained by subtracting the fitted air and air/CO absorption spectra. The CO sensing signal is defined as the peak to peak difference between points A and B on the difference spectrum.

Figure 2 displays the resulting CO sensing signal as a function of time for the Au-YSZ film upon exposure to 1, 0.75, 0.5, 0.25 and 0.1 vol.% CO concentrations in air at 500°C. The change in the absorption spectra upon exposure to CO was reversible, and the sensing signal increased with increasing CO concentration. A background signal of approximately 0.04 is observed during each of the air cycles and is attributed to the incomplete subtraction of the fitted spectra due to the noise levels observed in the raw data. The response time, i.e., the time required for the sensing signal to obtain its maximum value upon exposure to CO, was approximately 40 s at all CO concentrations, with recovery in the subsequent air pulse displaying a two-stage mechanism comprised of a fast, approximately 60 s, initial stage, followed by a slower, approximately 1000 s, stage.

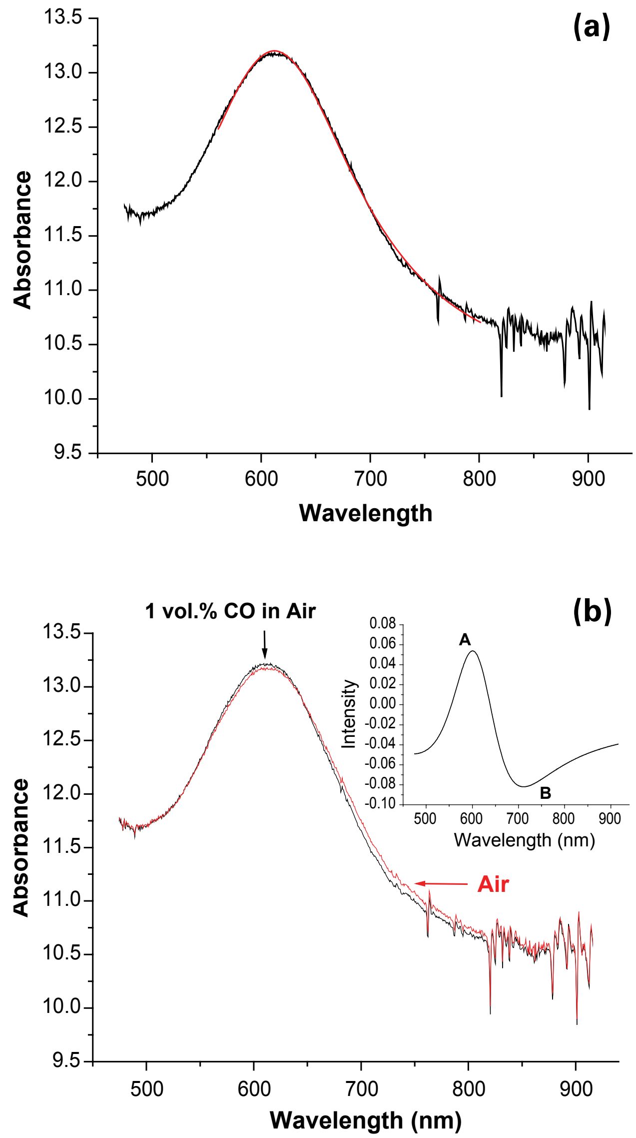

FIGURE 1. a) Absorbance spectra of the Au-YSZ nanocomposite film in air at 500°C with a corresponding Lorentzian curve fit (red line).
b) Absorption spectra for air and 1 vol.% CO in air exposures at 500°C. The inset displays the difference spectrum obtained by subtracting the fitted data resulting from the air and the air/CO exposures.

Figure 3 reports the change in sensing signal, normalized to that observed for the 1 vol.% CO exposures, plotted versus CO concentration at 500°C. The data in Figure 3 were obtained from three individual runs and indicate a reproducible response towards CO at this temperature. The increase in signal was nearly

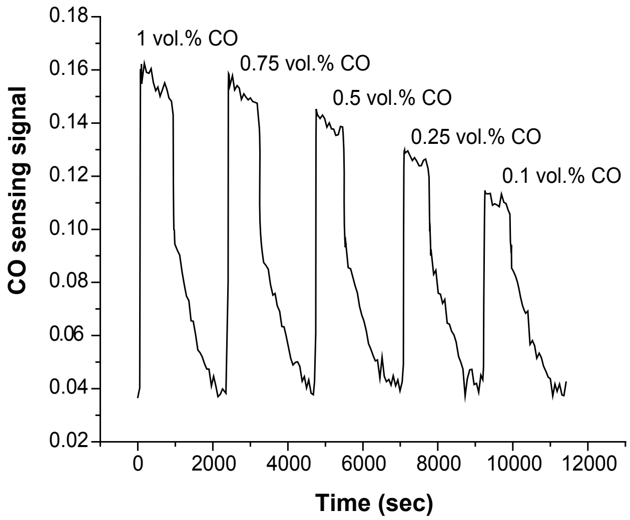

FIGURE 2. Sensing Signal Response Curve of the Au-YSZ Nanocomposite Film upon Exposure to 1, 0.75, 0.5, 0.25 and 0.1 vol.% CO in Air at 500°C

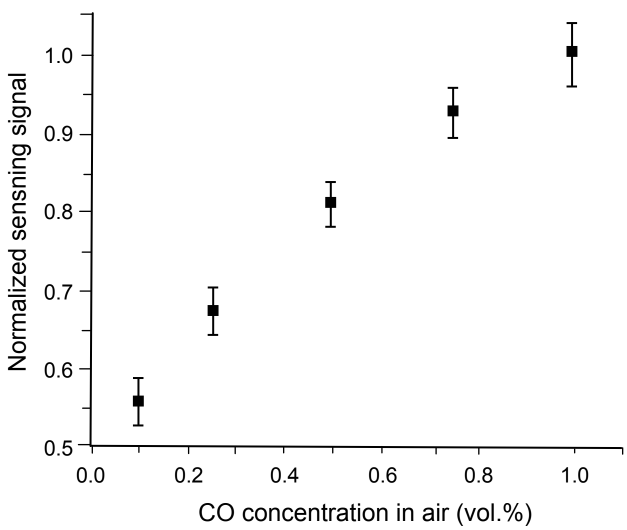

FIGURE 3. Normalized sensing signal change versus CO concentration at 500°C averaged over three separate exposure experiments. The signal at 1 vol.% CO in air was normalized to be unity.

linear over a CO concentration range between 0.1 and 1 vol.%. While this initial data set is promising for the potential development of an optical-based method for the detection of CO under harsh operating conditions, a complete set of reliability tests will be required and are underway to determine the long term operating characteristics of this nanocomposite material.

This behavior of the SPR band, upon exposure to CO, was not observed when using nitrogen as the carrier gas, indicating an oxygen dependent reaction mechanism. Additionally, the SPR band showed no measurable signal change upon exposure to CO at temperatures below approximately 400°C. The oxygen and temperature dependent characteristics, coupled with the oxygen ion conduction properties of the YSZ matrix are indicative of charge transfer reactions occurring at the 3-phase boundary region between oxygen, Au and YSZ, which result in charge transfer into the Au nanoparticles. These reactions are associated with the oxidation of CO, and a corresponding reduction of the YSZ matrix. The chemical reaction induced charge injection into the Au nanoparticles results in the observed blue shift and narrowing of the SPR band.

Conclusions

- The nanocomposite films exhibited an SPR absorption band around 600 nm, which upon exposure to CO in an air ambient at 500°C underwent a reversible blue shift and a narrowing of the full width half maximum.
- The change in the SPR band increased linearly with increasing CO concentration in the range between 0.1 to 1 vol.%.
- The presence of O_2 and sufficiently high temperatures for oxygen ion transport in YSZ were confirmed to be essential elements for the sensing mechanism.
- The behavior of the SPR band upon exposure to CO in the presence of air, was attributed to changes both in the free electron density of the Au nanoparticles and in the interfacial chemistry due to reactions associated with the reduction of the YSZ matrix and oxidation of CO.

FY 2006 Publications/Presentations

1. "Development and Characterization of Au-YSZ Surface Plasmon Resonance Based Sensing Materials: High Temperature Detection of CO", George Sirinakis, Rezina Siddique, Ian Manning, Philip H. Rogers, Michael A. Carpenter, accepted to *J. Phys. Chem. B.*

2. "All-optical Detection of CO and NO_2 at High Temperatures by Au-YSZ Nanocomposites", G. Sirinakis, R. Siddique, P. H. Rogers, I. Manning, M. A. Carpenter, Materials Research Society Meeting, Spring 2006.